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(54) SURFACE COATING METHOD BY ELECTROLYTIC  
 POLYMERIZATION

(71) We, TOYOTA JIDOSHA KOGYO KABUSHIKI KAISHA, a Corporation duly organised and existing under the laws of Japan, having its principal place of business at 1, Toyota-cho, Toyota-shi, Aichi-ken, Japan do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to the coating of articles by electrolytic polymerization.

The industrial applications of electrophoretic coating have become widespread. According to this coating method, an electroconductive object is coated through electrolysis, electrophoresis, electrodeposition and electroendosmosis in a pre-polymer solution of certain molecular weight.

In the case of electrophoretic coating, several steps are involved such as washing with water, air-blowing, heating and drying, and removal of excess treatment chemicals from the treatment vessel. Moreover, the coating material must be preliminarily polymerized.

In the case of electrolytic polymerization, however, both film formation and polymerization of a monomer material can be carried out simultaneously. In the conventional coating method by electrolytic polymerization, a direct current is passed through a monomer electrolyte solution, and as a result a polymer film is formed on the electrode surface (usually cathode), while at the same time polymerization takes place in the solution. As a result the monomer in the electrolyte is consumed other than in the formation of the coating, thereby causing troubles, retarded formation of film and making it necessary to remove the polymer thus formed from the electrolyte.

According to the present invention, there is provided a method of simultaneously

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polymerizing a monomer, and coating the so formed polymer on an article to be coated, which method comprises passing an electric current through an electrolyte bath comprising:—

a vinyl or vinylidene monomer, an organic solvent therefor;

a supporting electrolyte to enhance the electroconductivity of said bath;

at least one additive compound selected from lower (C=1-5) straight chained alcohols, quinones and mercaptans.

in which the article to be coated forms the cathode.

In the method of the present invention a polymerized coating of vinyl or vinylidene polymer is formed on an object to be coated and at the same time, the formation of a polymer in the electrolyte solution is inhibited by the additive compound.

A vinyl compound which may be an acrylic acid or an acrylic ester may be dissolved in an organic solvent and introduced into an electrolytic vessel. To improve the electroconductivity of this solution, a supporting electrolyte is added. The additive selected from a lower (C=1-5) straight chain alcohol, a mercaptan or a quinone is then added to the solution.

An electroconductive anode and an object to be coated as cathode, are immersed in the electrolyte solution and a rectified current is passed through the solution. After a preset time, the electrodes are lifted from the bath for air-drying or drying by heat.

The vinyl or vinylidene compound may be methacrylonitrile, methylmethacrylate, acrylonitrile, ethylacrylate, methyl vinyl ketone, acrylamide, 2-hydroxyethylmethacrylate, glycidylacrylate, glycidylmethacrylate, styrene, divinyl sulfone, N,N'-methylene-bisacrylamide, ethylene glycol dimethacrylate, methylacrylate and ethylmethacrylate. The organic solvent may be

selected from dimethylsulfoxide, dimethylacetamide, dimethylformamide, dioxane, acetonitrile, benzene, toluene and xylene.

Useful additives are: Lower straight

- 5 chain alcohols such as methyl alcohol, ethyl alcohol, propyl alcohol, n-butyl alcohol, and n-amyl alcohol; quinones such as benzoquinone, hydroquinone, phenanthraquinone, 2,5-dimethylquinone, and tetrachloro benzoquinone; sulfur containing compounds such as methyl mercaptan, ethylmercaptan, propylmercaptan, butylmercaptan, benzylmercaptan and thiophenols.

- 15 As the present invention is performed using the additive, polymerization in the solution is inhibited and this permits effective utilization of the monomer and negates the need for removal of polymer from the electrolyte solution. Also, the concentration of the monomer in the solution can be regulated in terms of the total area of coating.

#### Reference Example

- 25 When the current at a density of 2 mA/cm<sup>2</sup> is passed for 5 minutes through the following composition;

Methacrylonitrile	...	...	50 g
Dimethylacetamide	...	...	50 g
McKee's salt	...	...	0.5 g

- 30 (Tetraethylammonium-p-toluenesulfonate) in a stream of nitrogen at 25°C., with a carbon rod as the anode and a 12 cm<sup>2</sup> aluminum plate as the cathode, a yellow coat of 0.28 g polymethacrylonitrile is formed on the aluminum plate. At the same time 0.063 g of polymethacrylonitrile is added to the solution. With further passage of current it accumulates, resulting in the monomer being consumed other than in the formation of the coating. In this case, the polymer on the coated surface is determined, by weighing the surface to be coated before and after polymerization; while the amount of polymer in the solution is determined by pouring the electrolyte solution used for polymerization into methanol, crystallizing, filtering and drying it.

- 50 Following is a description by way of example only of methods of carrying the invention into effect:—

#### Example 1

Using the following composition:

- |                      |     |     |       |
|----------------------|-----|-----|-------|
| Methacrylonitrile    | ... | ... | 50 g  |
| 55 Dimethylacetamide | ... | ... | 50 g  |
| McKee's salt         | ... | ... | 0.5 g |
| Ethanol              | ... | ... | 0.4 g |

- and under the same conditions as in the reference example, polymerization is carried out, to produce a coating of 0.18 g on the aluminum plate. The amount of polymethacrylonitrile in the solution is only 0.004 g. This volume, as converted in terms of polymer weight in the solution against the weight of the coating, corresponds to

about 1/10 of the value in the reference example.

#### Example 2

Using the following composition:

Methacrylonitrile	...	...	50 g	70
Dimethylacetamide	...	...	50 g	
McKee's salt	...	...	0.5 g	
n-amylalcohol	...	...	0.4 g	

and under the same conditions as in the reference example, polymerization is carried out. The weight of the coating is 0.25 g and the polymer in the solution is 0.004 g. This volume, as converted in terms of polymer weight in the solution against the weight of the coating, corresponds to about 1/17 of the value in the reference example.

#### Example 3

Using the following composition:

Methacrylonitrile	...	...	50 g	
Dimethylacetamide	...	...	50 g	85
McKee's Salt	...	...	0.5 g	
p-Benzoquinone	...	...	0.5 g	

and under the same conditions as in the reference example, polymerization is carried out to produce a yellow coating of 0.27 g polymethacrylonitrile on the aluminum plate, and 0.049 g of a polymer occurs in the solution. As converted in terms of polymer weight in the solution against the weight of the coating, this is equivalent to about 4/5 of the value in the reference example.

#### Example 4

Using the following composition:

Methacrylonitrile	...	...	50 g	
Dimethylacetamide	...	...	50 g	100
McKee's salt	...	...	0.5 g	
Ethylmercaptan	...	...	0.4 g	

and under the same conditions as in the reference example, polymerization is carried out to produce a coating of 0.26 g on the aluminum plate. Thereby, the amount of a polymer in the solution is only 0.012 g. As converted in terms of the polymer weight in the solution against the weight of the coating, this is equivalent to about 1/5 of the value in the reference example.

#### Example 5

Using the following composition:

Methacrylonitrile	...	...	50 g	
Dioxane	...	...	50 g	115
McKee's salt	...	...	0.5 g	
n-amylalcohol	...	...	0.4 g	

and under the same conditions as in the reference example, polymerization is carried out to produce a coating of 1.5 g on the aluminum plate and 0.50 g of a polymer occurs in the solution. When in this case n-amylalcohol is not added, the coat will be 1.4 g and the polymer in the solution will amount to 0.60 g. Through addition of n-amylalcohol, the value as converted in terms of polymer weight in the solution against the weight of the coating will be reduced to about 7/10 of the value obtained when the n-amylalcohol was not present.

*Example 6*

Using the following composition:

- |   |                    |       |
|---|--------------------|-------|
|   | Methylmethacrylate | 50 g  |
|   | Dimethylacetamide  | 50 g  |
| 5 | McKee's salt       | 0.5 g |
|   | n-propylalcohol    | 0.4 g |
- and under the same conditions as in the reference example, polymerization is carried out to produce a coating of 3.1 g on the cathode plate. The polymer in the solution is 0.16 g. When in this case n-propylalcohol is not added, the coating will be 3.1 g and in the polymer in the solution is 0.31 g. Through addition of n-propylalcohol, the value as converted in terms of polymer weight in the solution against the weight of the coating is reduced to about one-half.

*Example 7*

Using the following composition:

- |  |                   |       |
|--|-------------------|-------|
|  | Methylvinylketone | 50 g  |
|  | Dimethylacetamide | 50 g  |
|  | McKee's salt      | 0.5 g |
|  | Ethylmercaptan    | 0.5 g |
- and under the same conditions as in the reference example, polymerization is carried out to produce a coating of 1.8 g on the cathode plate and in the solution 0.25 g of a polymer occurs. When in this case ethylmercaptan is not added, the coating will be 1.7 g and in the polymer in the solution is 0.38 g. Through addition of ethylmercaptan, the value as converted in terms of polymer weight in the solution against the weight of the coating is reduced to about three fifths.

*Example 8*

Using the following composition:

- |    |                   |       |
|----|-------------------|-------|
|    | Methacrylonitrile | 20 g  |
| 40 | Glycidylacrylate  | 10 g  |
|    | Dimethylacetamide | 70 g  |
|    | McKee's salt      | 0.2 g |
|    | Thiophenol        | 0.5 g |
- and under the same conditions as in the reference but this time a current at a density of 5 mA/cm<sup>2</sup> is passed for 3 minutes, a copolymerized coating is produced on the aluminum plate. The weight of this coating is 0.32 g and 0.12 g of a polymer occurs in the solution. When thiophenol is not added in this case, the coating will be 0.36 g and the polymer in the solution is 0.34 g. Through addition of thiophenol, the value as converted in terms of polymer weight in the solution against the weight of the coating is reduced to about one-half.

*Example 9*

Using the following composition:

- |    |                      |       |
|----|----------------------|-------|
|    | Methacrylonitrile    | 15 g  |
| 60 | Methylmethacrylate   | 5 g   |
|    | Glycidylmethacrylate | 5 g   |
|    | Dimethylformamide    | 75 g  |
|    | McKee's Salt         | 0.2 g |
|    | Phenanthraquinone    | 0.5 g |
- and under the same conditions as in the

reference but with a current at a density of 4 mA/cm<sup>2</sup> passed for 5 minutes, a copolymerized coating is obtained on the aluminum plate. This coating weighs 0.73 g and the polymer in the solution is 0.31 g. When phenanthraquinone is not added in this polymerization, the coating will be 0.82 g and in the solution 0.68 g of polymer will occur. Through addition of phenanthraquinone, the value as converted in terms of polymer weight in the solution against the weight of the coating is reduced to about one-half.

*Example 10*

Using the following composition:

- |  |                      |       |
|--|----------------------|-------|
|  | Glycidylmethacrylate | 20 g  |
|  | Methylmethacrylate   | 20 g  |
|  | Dimethylsulfoxide    | 60 g  |
|  | McKee's salt         | 0.2 g |
|  | Methanol             | 0.2 g |

and under the same conditions as in the reference but with a current at a density of 5 mA/cm<sup>2</sup> passed for 4 minutes, a copolymerized coating is formed on the aluminum plate. This coating weighs 0.46 g, and simultaneously 0.08 g of a polymer occurs in the solution. When methanol is not added in this case, the coating will be 0.50 g and the polymer will be 0.26 g in the solution. Accordingly, through addition of methanol, the value as converted in terms of polymer weight in the solution against the weight of the coating is reduced to about one third.

*Example 11*

Using the following composition:

- |  |                   |       |
|--|-------------------|-------|
|  | Methacrylonitrile | 20 g  |
|  | Ethylacrylate     | 20 g  |
|  | Dimethylformamide | 60 g  |
|  | McKee's salt      | 0.2 g |
|  | Benzylmercaptan   | 0.5 g |

and under the same conditions as in the reference but with a current at a density of 4 mA/cm<sup>2</sup> passed for 5 minutes, a copolymerized coating is formed on the aluminum plate. The weight of this coating is 0.32 g, and simultaneously 0.13 g of a polymer occurs in the solution. When benzylmercaptan is not added to this system, the coating will be 0.36 g and the polymer in the solution weighs 0.42 g. Through addition of benzylmercaptan, the value as converted in terms of polymer weight in the solution against the weight of the coating is reduced to about one-half.

*Example 12*

Using the following composition:

- |  |                      |       |
|--|----------------------|-------|
|  | Acrylonitrile        | 15 g  |
|  | Methylacrylate       | 25 g  |
|  | Dimethylacetamide    | 60 g  |
|  | McKee's salt         | 0.2 g |
|  | 2, 5-dimethylquinone | 0.5 g |

and under the same conditions as in the reference but with a current at a density of 5 mA/cm<sup>2</sup> passed for 3 minutes, a copoly-

merized coating is formed on the aluminum plate. The weight of this coating is 0.48 g and simultaneously 0.10 g of a polymer occurs in the solution. When 2,5-dimethylquinone is not added to this system, the coating will be 0.52 g and the polymer in the solution will be 0.43 g. Through addition of 2,5-dimethylquinone, the value as converted in terms of polymer weight in the solution against the weight of the coating is reduced to about one quarter.

#### Example 13

Using the following compositions:

	Methacrylonitrile	20 g
15	Ethylmethacrylate	30 g
	Dimethylformamide	50 g
	McKee's salt	0.2 g
	Butylmercaptan	0.5 g

and under the same conditions as in the reference but with a current at a density of 5 mA/cm<sup>2</sup> passed for 3 minutes, a copolymerized coating is formed on the aluminum plate. The weight of this coating is 0.36 g, and simultaneously 0.16 g of a polymer occurs in the solution. Without addition of butylmercaptan to this system, the weight of the coating will be 0.40 g and 0.38 g of a polymer will occur in the solution. Through addition of butylmercaptan, the value as converted in terms of polymer weight in the solution against the weight of the coating is reduced to about one-half.

#### Example 13

Using the following composition:

35	Acrylonitrile	10 g
	N-N'-methylene-bis-acrylamide	5g
	Dimethylformamide	85 g
	McKee's salt	0.2 g

and under similar conditions as in the reference example, the current at a density of 8 mA/cm<sup>2</sup> is passed for 3 minutes and as a result a copolymerized cross linking coating is formed on the aluminum plate. The coating weighs 0.28 g and at the same time 0.68 g of a polymer occurs in the solution. If 0.4 g of n-propylalcohol is added to this system for polymerization, the coating will be 0.29 g and the polymer in the solution will be 0.40 g. Thus, through addition of n-propylalcohol, the value as converted in terms of polymer weight in the solution against the coating weight is reduced to about one-half.

#### Example 15

Using the following composition:

55	Methacrylonitrile	20 g
	Glycidylmethacrylate	20 g
	Methylmercaptan	5 g
	Dimethylacetamide	55 g
60	McKee's salt	0.2 g

and under similar conditions as in the reference, the current at a density of 5 mA/cm<sup>2</sup> is passed for 4 minutes. As a result a copolymerized cross linking coating is formed on the aluminum plate. The coating

weighs 0.34 g and at the same time 0.42 g of a polymer occurs in the solution. If 0.5 g of tetrachloro benzoquinone is added to this system, the coating will be 0.36 g and the polymer in the solution will be 0.10 g. Thus, through addition of tetrachloro benzoquinone, the value as converted in terms of polymer weight in the solution against the coating weight is reduced to about one-fifth.

#### Example 16

Using the following composition:

	Methylmethacrylate	45 g
	Ethylene glycol dimethacrylate	15 g
	Dimethylacetamide	40 g
	McKee's salt	0.5 g

and under similar conditions as in the reference, the current at a density of 5 mA/cm<sup>2</sup> is passed for 3 minutes. As a result, a copolymerized cross linking coating is formed on the aluminum plate. The coating weighs 0.36 g and at the time 0.38 g of a polymer occurs in the solution. On the other hand, if 0.5 g of methylmercaptan is added to this system, then the coating will be 0.40 g and the polymer in the solution will be 0.08 g. Thus, through addition of methylmercaptan, the value as converted in terms of polymer weight in the solution against the coating weight is reduced to about one-fifth.

#### WHAT WE CLAIM IS:—

1. A method of simultaneously polymerizing monomer, and coating the so formed polymer on an article to be coated, which method comprises passing an electric current through an electrolyte bath comprising:

- a vinyl or vinylidene monomer, an organic solvent therefor;
- a supporting electrolyte to enhance the electroconductivity of said bath;
- at least one compound selected from lower (C=1-5) straight chained alcohols, quinones and mercaptans

in which the article to be coated forms the cathode.

2. A method as claimed in claim 1 wherein the electric current is a rectified current.

3. A method as claimed in either of the preceding claims wherein the vinyl or vinylidene compound is selected from methacrylonitrile, methylmethacrylate, acrylonitrile, ethylacrylate, acrylamide, 2-hydroxyethylmethacrylate, glycidylacrylate, glycidylmethacrylate, styrene, divinyl sulfone, N,N'-methylene-bis-acrylamide, ethylene glycol dimethacrylate, methylacrylate and ethylmethacrylate.

4. A method as claimed in any preceding claim wherein the solvent is selected from dimethylsulfoxide, dimethylacetamide, dimethylformamide, acetonitrile, benzene, toluene and xylene.

5. A method as claimed in any preceding claim wherein the lower straight chain alcohol is selected from methyl alcohol, ethyl alcohol, propyl alcohol, n-butyl alcohol and n-amyl alcohol.

6. A method as claimed in any one of claims 1 to 5 wherein the quinones are selected from benzoquinone, hydroquinone, phenanthraquinone, 2,5 - dimethylquinone, and tetrachloro benzoquinone.

7. A method as claimed in any one of claims 1 to 6 wherein the sulphur containing compound is selected from methylmercaptan, ethylmercaptan, propylmercaptan, butylmercaptan, benzylmercaptan and thiophenols.

8. A method of coating an article by electrolytic polymerization as claimed in claim 1 and substantially as described in any one of the specific examples hereinbefore set forth.

9. Articles whenever coated by the method claimed in any preceding claims.

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